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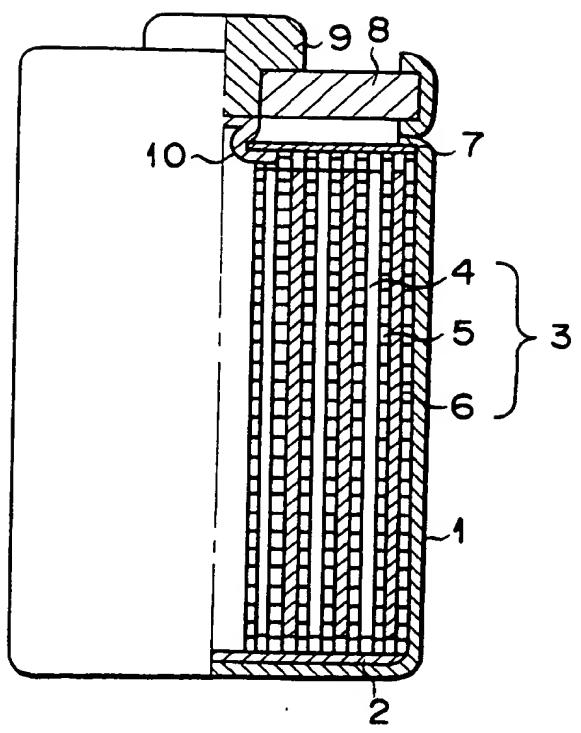
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(54) A nonaqueous electrolyte secondary battery.

(57) A nonaqueous electrolyte secondary battery having an enhanced capacity and a long charge/discharge cycle life is disclosed. The nonaqueous electrolyte secondary battery comprises a positive electrode (4) housed in a case (1) and containing a chalcogen compound as an active material, a negative electrode (6) arranged in the case (1) such that a separator (5) is sandwiched between the positive and negative electrodes (4, 6) and containing a carbonaceous material as an active material that absorbs and discharges lithium ions and a nonaqueous electrolyte contained in the case (1) and prepared by dissolving 0.5 mol/l to 1.5 mol/l of electrolytic salt selected from the group consisting of LiPF₆, LiBF₄, LiAsF₆ and LiCF₃SO₃ in a solvent mixture comprising at least one first nonaqueous solvent selected from the group consisting of noncyclic carbonate, cyclic carbonate, γ-butyrolactone and acetonitrile and at least one second nonaqueous solvent containing selected from the group consisting of 1,2-diethoxyethane, 1,2-dimethoxyethane, 1,2-ethoxymethoxyethane, 1,3-dimethoxypropane, diethyl ether and tetrahydrofuran, the amount of the second nonaqueous solvent in the solvent mixture being so determined that the mol ratio ([S]/[Li]) of the second nonaqueous solvent [S] to lithium ions [Li] is 0.5 to 3.



F I G. 1

The present invention relates to a nonaqueous electrolyte secondary battery and, more particularly, to a nonaqueous electrolyte secondary battery containing an improved a nonaqueous electrolyte.

In recent years, a nonaqueous electrolyte battery has attracted attention as a high energy density battery. Of such nonaqueous electrolyte batteries, a primary battery using a light metal such as lithium, sodium, or aluminum as a negative electrode active material and manganese dioxide (MnO_2), carbon fluoride [(CF)_n], thionyl chloride ($SOCl_2$), or the like as a positive electrode active material is already widely used as a power source of a timepiece or a backup battery of a memory.

In addition, as the sizes and weights of various types of electronic equipment such as communication equipment have been decreased, a demand for a secondary battery having a high energy density which can be suitably used as a power source of such equipment has been increased, and a nonaqueous electrolyte secondary battery has been actively studied. For example, a nonaqueous electrolyte secondary battery using lithium as a negative electrode and an electrolyte prepared by dissolving an electrolytic salt such as $LiClO_4$, $LiBF_4$, $LiAsF_6$, or $LiPF_6$ in a nonaqueous solvent such as propylene carbonate (PC), 1,2-dimethoxyethane (DME), γ -butyrolactone (γ -BL), or tetrahydrofuran (THF) has been studied. In addition, a compound which topochemically reacts with lithium such as TiS_2 , MoS_2 , V_2O_5 , or V_6O_{13} has been studied as a positive electrode material.

The above secondary battery, however, has not been put into practical use yet. This is mainly because a charge/discharge efficiency of the battery is low and its number of charge/discharge times or cycle life is short. The reason for this is assumed that lithium as a negative electrode is degraded due to a reaction with an electrolyte. That is, lithium dissolved in an electrolyte as lithium ions upon discharge reacts with a solvent and its surface is partially deactivated when it precipitates upon charge. Therefore, when charge/discharge is repeated, lithium is precipitated in the form of dendrites or small spheres, or is separated from a collector.

On the other hand, nonaqueous electrolyte secondary batteries realized by utilizing a carbonaceous material that can absorbed and discharge lithium to be used as an active material of a negative electrode are disclosed in U.S. Patent Nos. 4,668,595 and 4,702,977. The U.S. Patent No. 4,668,595 also describes the use of tetrahydrofuran, γ -butyrolactone, dimethoxyethane, propylene carbonate, ethylene carbonate or a mixture thereof as a nonaqueous solvent for preparing a nonaqueous electrolyte.

It is the object of the present invention to provide a nonaqueous electrolyte secondary battery that has a negative electrode which is capable of sufficiently absorbing and discharging lithium and can effectively

suppress any degradation of the nonaqueous electrolyte contains in it and that of the negative electrode by the nonaqueous electrolyte, thereby enhancing the overall capacity and improving charge/discharge cycle life.

According to the invention, there is provided a nonaqueous electrolyte secondary battery comprising a positive electrode housed in a case and containing a chalcogen compound as an active material, a negative electrode arranged in the case in which a separator is sandwiched between the positive and negative electrodes and containing as an active material a carbonaceous material for absorbing and discharging lithium ions and a nonaqueous electrolyte housed in the case, the nonaqueous electrolyte is prepared by dissolving 0.5 mol/l to 1.5 mol/l of an electrolytic salt selected from the group consisting of lithium phosphate hexafluoride ($LiPF_6$), lithium borofluoride ($LiBF_4$), lithium arsenate hexafluoride ($LiAsF_6$) and lithium trifluorometasulfonate ($LiCF_3SO_3$) in a solvent mixture comprising at least one first nonaqueous solvent selected from the group consisting of noncyclic carbonate, cyclic carbonate, γ -butyrolactone and acetonitrile and at least one second nonaqueous solvent selected from the group consisting of 1,2-dimethoxyethane, 1,2-dimethoxyethane, 1,2-ethoxymethoxyethane, 1,3-dimethoxypropane, diethylether and tetrahydrofuran and that the amount of the second nonaqueous solvent in the solvent mixture is so determined that the mol ratio ([S]/[Li]) of the second nonaqueous solvent [S] to lithium ions [Li] is 0.5 to 3.

This invention can be more fully understood from the following detailed description when taken in conjunction with the accompanying drawings, in which:

Fig. 1 is a partial sectional view showing a nonaqueous electrolyte secondary battery according to the present invention;

Fig. 2 is a graph showing a change in discharge capacity as a function of a cycle number in a nonaqueous electrolyte secondary battery of each of Examples 1 to 5 and Controls 1 and 2; and Fig. 3 is a graph showing a change in discharge capacity as a function of a cycle number in a nonaqueous electrolyte secondary battery of each of Examples 6 to 10 and Controls 3 and 4.

A nonaqueous electrolyte secondary battery according to the present invention will be described below with reference to Fig. 1.

Referring to Fig. 1, a cylindrical case 1 having a bottom houses an insulator 2 arranged on its bottom and electrodes 3. The electrodes 3 have a structure in which a band-like member obtained by stacking a positive electrode 4, a separator 5, and a negative electrode 6 in the order named is spirally wound so that the negative electrode 6 is located outside. The case 1 contains a nonaqueous electrolyte. Insulating paper 7 having an opening formed in its central portion is placed above the electrodes 3 housed in the

case 1. An insulating opening sealing plate 8 is arranged at an upper opening portion of the case 1 and liquid-tightly fixed to the case 1 by calking the upper opening portion inwardly. A positive terminal 9 is fitted in the center of the plate 8. One end of a positive lead 10 is connected to the positive electrode 4 and the other end to the positive terminal 9. The negative electrode 6 is connected to the case 1 as a negative terminal via a negative lead (not shown).

The case 1 is typically made of stainless steel.

The positive electrode 4 contains a chalcogen compound as an active material. More specifically, the positive electrode 4 is realized by preparing a mixture of the chalcogen compound, an organic binder material and a conductive material, kneading the mixture into a sheet and pressing it against a current collector member.

Example of the chalcogen compound are manganese dioxide, a lithium-manganese composite oxide, a lithium cobalt oxide, a lithium nickel cobalt oxide, lithium containing non-crystalline vanadium pentaoxide, titanium disulfide and molybdenum disulfide. Of these, the lithium cobalt oxide is particularly advantageous as it can raise the potential of the positive electrode and hence the voltage of the battery.

Example of the organic binder material is polytetrafluoroethylene. Examples of the conductive material are acetylene black and graphite. The current collector member is used of aluminum foil, stainless steel foil and nickel foil.

The negative electrode 6 contains as an active material a carbonaceous material for absorbing and discharging lithium ions. Specifically, the negative electrode 6 is realized by preparing a mixture of the carbonaceous material and an organic binder material and applying the mixture to a current collector member to coat the latter with the former.

Examples of the carbonaceous material are coke, sintered synthetic resin, carbon fiber, thermally decomposable gaseous carbon, mesophase pitch-like carbon and mesocarbon microbeads. The carbonaceous material may have been charged with lithium ions in advance. When the chalcogen material such as titanium disulfide no containing lithium at all is used, the carbonaceous material charged with lithium ions is particularly preferable.

Example of the organic binder material is an ethylene-propylene copolymer. The current collector member is used of copper foil, nickel foil or stainless steel foil.

The nonaqueous electrolyte is typically prepared by dissolving an electrolytic salt into a solvent mixture, which will be described in detail below.

Example of the electrolytic salt are LiPF₆, LiBF₄, LiAsF₆ and LiCF₃SO₃. When the battery is excessively charged, the electrolytic salt is less likely oxidative destruction than lithium perchlorate (LiClO₄) which is normally used for conventional nonaqueous

electrolyte secondary batteries. LiPF₆ is particularly advantageous because of its high molar conductivity. The electrolytic salt should be dissolved in the solvent mixture in amount of 0.5 mol/l to 1.5 mol/l. The dissolution amount of the electrolytic salt in the solvent mixture is limited for following reason. That is, if the dissolution amount of the electrolytic salt is less than 0.5 mol/l, the conductivity of the nonaqueous electrolyte can not be increased. If the dissolution amount of the electrolytic salt is 1.5 mol/l or more, the conductivity of the nonaqueous electrolyte can not be increased and its chemical stability is decreased. The dissolution amount of the electrolytic salt is preferably 0.75 mol/l to 1.25 mol/l.

The solvent mixture comprises at least one first nonaqueous solvent selected from group consisting of noncyclic carbonate, cyclic carbonate, γ-butyrolactone and acetonitrile and at least one second nonaqueous solvent selected from group consisting of 1,2-diethoxyethane, 1,2-dimethoxyethane, 1,2-ethoxymethoxyethane, 1,3-dimethoxypropane, diethylether and tetrahydrofuran.

The first nonaqueous solvent has a high dielectric constant and is capable of dissolving the electrolytic salt. Examples of the noncyclic carbonate are dimethylcarbonate and diethylcarbonate. Examples of the cyclic carbonate are ethylenecarbonate, propylenecarbonate and butylenecarbonate. Preferable the first nonaqueous solvent is mixture of ethylenecarbonate and propylenecarbonate or mixture of propylenecarbonate and diethylcarbonate.

The second nonaqueous solvent has low viscosity and increases the conductivity of the nonaqueous electrolyte. Of the candidate compounds of the second nonaqueous solvent, 1,2-diethoxyethane is recommended because it have a higher flash point than 1,2-dimethoxyethane and hence is convenient to handle.

The amount of the second nonaqueous solvent in the nonaqueous electrolyte is so determined that the mol ratio ([S]/[Li]) of the second nonaqueous solvent [S] to lithium ions [Li] is 0.5 to 3. The mol ratio is limited for following reason. That is, if the mol ratio is less than 0.5, the viscosity of the nonaqueous electrolyte undesirably rises to reduce its conductivity. If the mol ratio is 3 or more, the viscosity of the nonaqueous electrolyte is reached to increase its conductivity, although the capacity of the negative electrode to absorb and discharge lithium ions is reduced and the duration of effective charge/discharge cycles is curtailed. The mol ratio [S]/[Li] is preferably 1 to 2.

A nonpolar benzene or tolen may be added to the nonaqueous electrolyte by less than 30 vol% in order to reduce the viscosity of the nonaqueous electrolyte having a composition as described above.

In the secondary battery of the present invention, positive and negative electrodes each containing a specified active material are housed in a case with a

separator interposed between these electrodes. It should be noted that the nonaqueous electrolyte described above, which is housed in the case, permits increasing the amount of absorption and discharge of lithium ions performed by the carbonaceous material used as an active material of the negative electrode, leading to a high charge/discharge efficiency. This makes it possible to obtain a nonaqueous electrolyte secondary battery of a high capacity and a long cycle life.

The carbonaceous material used as an active material of the negative electrode absorbs lithium ions present in the nonaqueous electrolyte. In this case, the periphery of the lithium ion is selectively coordinated by the nonaqueous solvent having a large donor number, with the result that the nonaqueous solvent is taken up together with the lithium ion between adjacent carbon atoms of the carbonaceous material. It follows that the absorbed amount of lithium ions and the behavior of the decomposition reaction of the nonaqueous solvent are changed depending on the size and molecular weight of the coordinating nonaqueous solvent as well as by the number of coordinations. As described previously, the nonaqueous electrolyte used in the present invention is provided by a solvent mixture consisting of the first nonaqueous solvent such as propylene carbonate and the second nonaqueous solvent such as 1,2-dimethoxyethane. Since the donor number of the second nonaqueous solvent is larger than that of the first nonaqueous solvent, the lithium ion is selectively coordinated by the second nonaqueous solvent.

Such being the situation, it is important to determine appropriately the mixing amount of the second solvent. As described previously, nonaqueous electrolyte is prepared by dissolving 0.5 to 1.5 mol/l of the lithium salt in the solvent mixture. In the present invention, the mixing amount of the second solvent is determined in view of the lithium salt-dissolving capability of the solvent mixture such that the molar ratio ([S]/[Li]) of the second solvent [S] to the lithium ion [Li] falls within a range of between 0.5 and 3. Where the molar ratio ([S]/[Li]) falls within the range defined in the present invention, it is possible to diminish the amounts of the second solvent and the lithium ion taken up between adjacent carbon atoms of the carbonaceous material acting as the active material of the negative electrode. In addition, the function of the second nonaqueous solvent to improve the conductivity of the nonaqueous electrolyte is not impaired. It follows that the amount of the lithium ions absorbed by and charged from the carbonaceous material can be increased. Further, it is possible to suppress the decomposition by the reducing reaction within the carbonaceous material and the intercalation into the carbonaceous material, with the result that it is possible to suppress the deterioration in the surface and crystal structure of the carbonaceous material during the

charge/discharge cycles. Among the second nonaqueous solvents, 1,2-dimethoxyethane exhibits a relatively weak coordinating force relative to the lithium ion and, thus, is prominently effective for suppressing the deterioration of the carbonaceous material.

It should also be noted that the electrolyte dissolved in the solvent mixture used in the present invention, i.e., LiPF₆, LiBF₄, LiAsF₆ or LiCF₃SO₃, is less likely to be decomposed by oxidation when the battery is excessively charged, compared with the conventional electrolyte of LiClO₄. Thus, the lithium salt specified in the present invention as the electrolyte permits suppressing the deterioration of the nonaqueous electrolyte during the charge/discharge cycles.

To reiterate, the amount of the lithium ions absorbed by and released from the carbonaceous material providing the active material of the negative electrode can be increased in the present invention. Also, the present invention permits suppressing the structural deterioration of the negative electrode and also permits suppressing the deterioration of the nonaqueous electrolyte. It follows that the present invention provides a nonaqueous electrolyte secondary battery of a large capacity and a long cycle life.

Now the present invention will be described in greater detail by way of examples that represents the best modes of carrying out the invention.

Example 1

80 wt% of a lithium cobalt oxide (Li_xCoO₂) powder, 15 wt% of acetylene black powder and 5 wt% of polytetrafluoroethylene powder were mixed to prepare a mixture and the mixture was applied to a current collector member made of aluminum foil to form a sheet-like positive electrode.

98 wt% of carbonaceous material powder obtained by sintering powdered phenol resin in nitrogen gas at 1,700°C for 2 hours and 2 wt% of ethylene-propylene copolymer were mixed to prepare a mixture and the mixture was applied to a current collector member made of nickel foil to form a sheet-like negative electrode.

The positive electrode, a separator formed a polypropylene porous film and the negative electrode were stacked in order named and spirally wound so that the negative electrode was located outside, thereby manufacturing electrodes.

In addition, 1.0 mol/l of LiPF₆ was dissolved in a solvent mixture consisting of ethylene carbonate, propylene carbonate and 1,2-dimethoxyethane (mixing volume ratio = 40:40:20) to prepare a nonaqueous electrolyte. The mol ratio ([S]/[Li]) of 1,2-dimethoxyethane [S] to lithium ions [Li] in the nonaqueous electrolyte was approximately 1.9.

The electrodes and the nonaqueous electrolyte were housed in a cylindrical stainless steel case hav-

ing a bottom to assemble the above-mentioned nonaqueous electrolyte secondary battery as showing in Fig. 1.

Example 2

1.0 mol/l of LiBF₄ was dissolved in a solvent mixture consisting of ethylene carbonate, propylene carbonate and 1,2-dimethoxyethane (mixing volume ratio = 40:40:20) to prepare a nonaqueous electrolyte. The resultant nonaqueous electrolyte and electrodes similar to those used in Example 1 were housed in a cylindrical stainless steel case having a bottom to assemble the nonaqueous electrolyte secondary battery shown in Fig. 1.

Example 3

1.0 mol/l of LiAsF₆ was dissolved in a solvent mixture consisting of ethylene carbonate, propylene carbonate and 1,2-dimethoxyethane (mixing volume ratio = 40:40:20) to prepare a nonaqueous electrolyte. The resultant nonaqueous electrolyte and electrodes similar to those used in Example 1 were housed in a cylindrical stainless steel case having a bottom to assemble the nonaqueous electrolyte secondary battery shown in Fig. 1.

Example 4

1.0 mol/l of LiPF₆ was dissolved in a solvent mixture consisting of ethylene carbonate, γ -butyrolactone and 1,2-dimethoxyethane (mixing volume ratio = 40:40:20) to prepare a nonaqueous electrolyte. The resultant nonaqueous electrolyte and electrodes similar to those used in Example 1 were housed in a cylindrical stainless steel having a bottom to assemble the nonaqueous electrolyte secondary battery shown in Fig. 1.

Example 5

1.0 mol/l of LiPF₆ was dissolved in a solvent mixture consisting of ethylene carbonate, propylene carbonate and tetrahydrofuran (mixing volume ratio = 40:40:20) to prepare a nonaqueous electrolyte. The mol ratio ([S]/[Li]) of tetrahydrofuran [S] to lithium ions [Li] in the nonaqueous electrolyte was approximately 2.5. The resultant nonaqueous electrolyte and electrodes similar to those used in Example 1 were housed in a cylindrical stainless steel case having a bottom to assemble the nonaqueous electrolyte secondary battery shown in Fig. 1.

Control 1

1.0 mol/l of LiPF₆ was dissolved in a solvent mixture consisting of ethylene carbonate and propylene

carbonate (mixing volume ratio = 50:50) to prepare a nonaqueous electrolyte. The resultant nonaqueous electrolyte and electrodes similar to those used in Example 1 were housed in a cylindrical stainless steel case having a bottom to assemble the nonaqueous electrolyte secondary battery shown in Fig. 1.

Control 2

10 1.0 mol/l of LiPF₆ was dissolved in a solvent mixture consisting of propylene carbonate and 1,2-dimethoxyethane (mixing volume ratio = 50:50) to prepare a nonaqueous electrolyte. The mol ratio ([S]/[Li]) of 1,2-dimethoxyethane to lithium ions [Li] in the nonaqueous electrolyte was approximately 4.8. The resultant nonaqueous electrolyte and electrodes similar to those used in Example 1 were housed in a cylindrical stainless steel case having a bottom to assemble the nonaqueous electrolyte secondary battery shown in Fig. 1.

15 20 Charge/discharge was repeatedly performed for each of the nonaqueous electrolyte secondary batteries of Examples 1 to 5 and Controls 1 and 2 with charge current of 50 mA to 4.2V and discharge current of 50 mA, and a discharge capacity and a cycle number each of battery were measured. The measurement results are shown in Fig. 2.

25 30 As seen from Fig. 2, the nonaqueous electrolyte secondary batteries of Examples 1 to 5 used a nonaqueous electrolyte having the mol ratio ([S]/[Li]) of 0.5 to 3 are showed a battery capacity and a cycle life much greater than those of the batteries obtained by Controls 1 and 2. In particularly, the battery of each of Examples 1, 3 and 5 has a high capacity and a very long cycle life.

Example 6

35 40 45 50 55 98 wt% of carbonaceous material powder consisting of mesocarbon microbeads and 2 wt% of ethylene-propylene copolymer were mixed to prepare a mixture, and the mixture was applied to an electric collector member made of nickel foil to form a sheet-like negative electrode. A positive electrode similar to it used in Example 1, a separator consisting of a polypropylene porous film and the negative electrode were stacked in the mentioned order and spirally wound so that the negative electrode was located outside, thereby manufacturing electrodes.

In addition, 1.0 mol/l of LiPF₆ was dissolved in a solvent mixture consisting of ethylene carbonate, propylene carbonate and 1,2-diethoxyethane (mixing volume ratio = 40:40:20) to prepare a nonaqueous electrolyte. The mol ratio ([S]/[Li]) of 1,2-diethoxyethane [S] to lithium ions [Li] in the nonaqueous electrolyte was approximately 1.5.

The electrodes and the nonaqueous electrolyte were housed in a cylindrical stainless steel case hav-

ing a bottom to assemble the nonaqueous electrolyte secondary battery shown in Fig. 1.

Example 7

1.0 mol/l of LiBF₄ was dissolved in a solvent mixture consisting of diethyl carbonate, propylene carbonate and 1,2-dimethoxyethane (mixing volume ratio = 20:60:20) to prepare a nonaqueous electrolyte. The resultant nonaqueous electrolyte and electrodes similar to those used in Example 6 were housed in a cylindrical stainless steel case having a bottom to assemble the nonaqueous electrolyte secondary battery shown in Fig. 1.

Example 8

1.0 mol/l of LiAsF₆ was dissolved in a solvent mixture consisting of ethylene carbonate, γ -butyrolactone and 1,2-dimethoxyethane (mixing volume ratio = 40:40:20) to prepare a nonaqueous electrolyte. The resultant nonaqueous electrolyte and electrodes similar to those used in Example 6 were housed in a cylindrical stainless steel case having a bottom to assemble the nonaqueous electrolyte secondary battery shown in Fig. 1.

Example 9

1.0 mol/l of LiPF₆ was dissolved in a solvent mixture consisting of propylene carbonate, diethyl carbonate and 1,2-dimethoxyethane (mixing volume ratio = 60:20:20) to prepare a nonaqueous electrolyte. The resultant nonaqueous electrolyte and electrodes similar to those used in Example 6 were housed in a cylindrical stainless steel case having a bottom to assemble the nonaqueous electrolyte secondary battery shown in Fig. 1.

Example 10

1.0 mol/l of LiPF₆ was dissolved in a solvent mixture consisting of diethyl carbonate, propylene carbonate and 1,2-ethoxymethoxyethane (mixing volume ratio = 20:60:20) to prepare a nonaqueous electrolyte. The mol ratio ([S]/[Li]) of 1,2-ethoxymethoxyethane [S] to lithium ions [Li] in the nonaqueous electrolyte was approximately 1.7. The resultant nonaqueous electrolyte and electrodes similar to those used in Example 6 were housed in a cylindrical stainless steel case having a bottom to assemble the nonaqueous electrolyte secondary battery shown in Fig. 1.

Control 3

1.0 mol/l of LiPF₆ was dissolved in a solvent mixture consisting of propylene carbonate and 1,2-dimethoxyethane (mixing volume ratio = 50:50) to prepare

a nonaqueous electrolyte. The mol ratio ([S]/[Li]) of 1,2-dimethoxyethane [S] to lithium ions [Li] in the nonaqueous electrolyte was approximately 4.8. The resultant nonaqueous electrolyte and electrodes similar to those used in Example 6 were housed in a cylindrical stainless steel case having a bottom to assemble the nonaqueous electrolyte secondary battery shown in Fig. 1.

Control 4

1.0 mol/l of LiPF₆ was dissolved in a solvent mixture consisting of propylene carbonate and 1,2-dimethoxyethane (mixing volume ratio = 50:50) to prepare a nonaqueous electrolyte. The mol ratio ([S]/[Li]) of 1,2-dimethoxyethane [S] to lithium ions [Li] in the nonaqueous electrolyte was 3.6. The resultant nonaqueous electrolyte and electrodes similar to those used in Example 6 were housed in a cylindrical stainless steel case having a bottom to assemble the nonaqueous electrolyte secondary battery shown in Fig. 1.

Charge/discharge was repeatedly performed for each of the nonaqueous electrolyte secondary battery of Examples 6 to 10 and Controls 3 and 4 with charge current of 120 mA to 4.2V and discharge current of 120 mA, and a discharge capacity and a cycle number each of battery were measured. The measurement results are shown in Fig. 3.

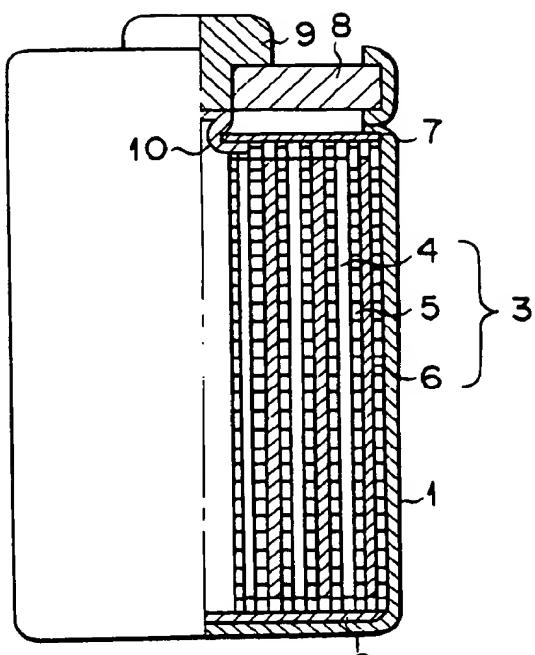
As seen from Fig. 3, the nonaqueous electrolyte secondary batteries of Examples 6 to 10 used a nonaqueous electrolyte having a mol ratio ([S]/[Li]) of 0.5 to 3 are showed a battery capacity and a cycle life much greater than those of the batteries obtained by Controls 3 and 4. In particularly, the battery of each of Examples 6, 8 and 10 has a high capacity and a very long cycle life.

As is apparent from the above description, a nonaqueous electrolyte secondary battery according to the present invention has an enhanced capacity and a long charge/discharge cycle life.

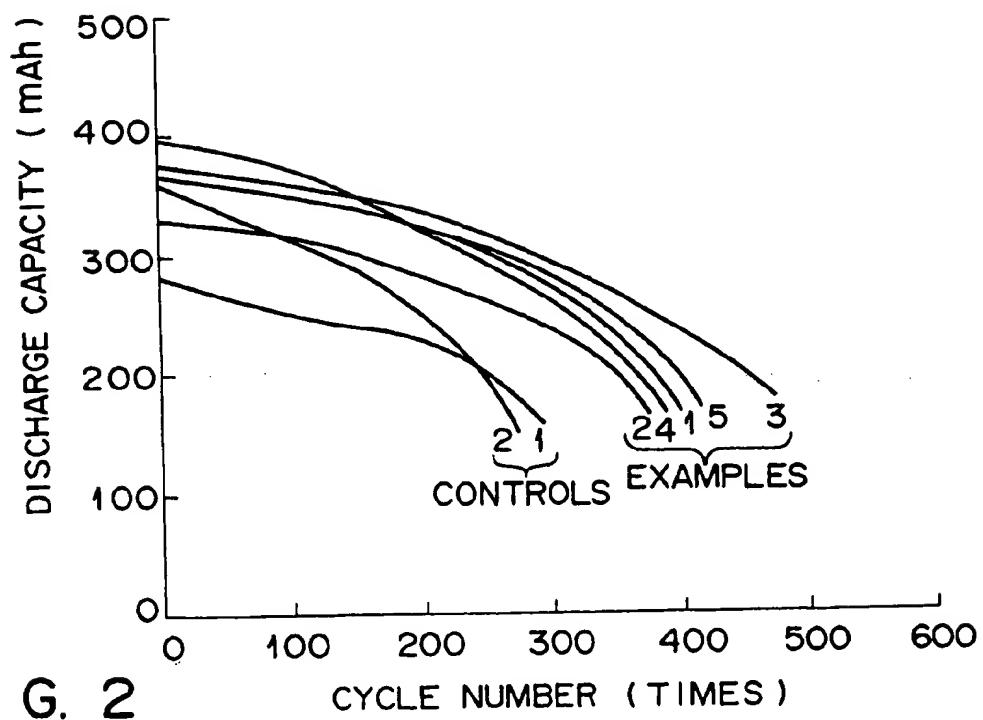
Claims

1. A nonaqueous electrolyte secondary battery characterized by comprising:
 - a positive electrode (4) housed in a case (1) and containing a chalcogen compound as an active material;
 - a negative electrode (6) arranged in the case (1) such that a separator (5) is sandwiched between the positive and negative electrodes (4, 6) and containing a carbonaceous material as an active material that absorbs and discharges lithium ions; and
 - a nonaqueous electrolyte contained in the case (1) and prepared by dissolving 0.5 mol/l to

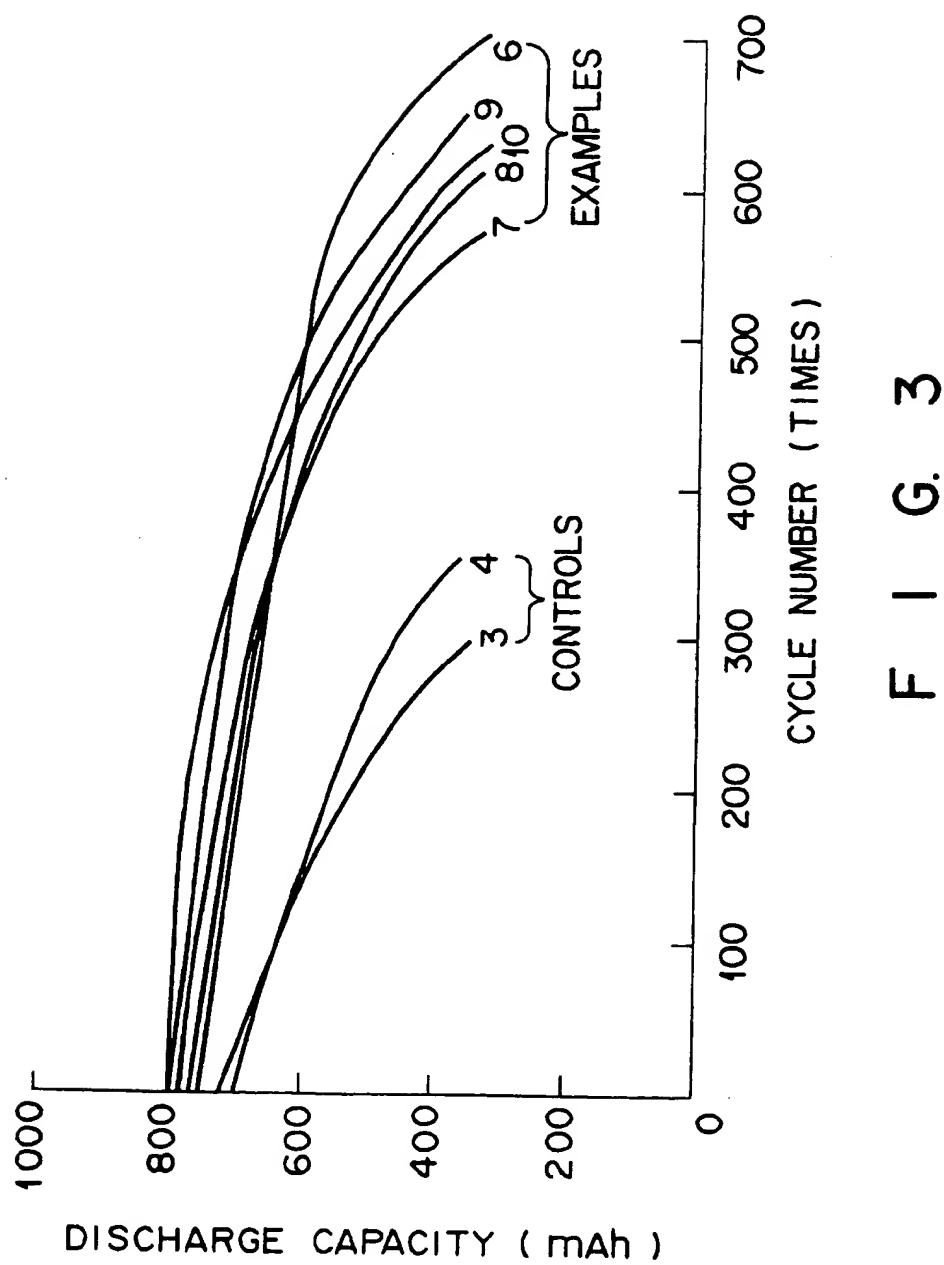
- 1.5 mol/l of an electrolytic salt selected from the group consisting of lithium phosphate hexafluoride (LiPF_6), lithium borofluoride (LIBF_4), lithium arsenate hexafluoride (LiAsF_6) and lithium trifluorometasulfonate (LiCF_3SO_3) in a solvent mixture comprising at least one first nonaqueous solvent selected from the group consisting of non-cyclic carbonate, cyclic carbonate, γ -butyrolactone and acetonitrile and at least one second nonaqueous solvent selected from the group consisting of 1,2-diethoxyethane, 1,2-dimethoxyethane, 1,2-ethoxymethoxyethane, 1,3-dimethoxypropane, diethylether and tetrahydrofurane, the amount of the second nonaqueous solvent in the solvent mixture being so determined that the mol ratio ([S]/[Li]) of the second nonaqueous solvent [S] to lithium ions [Li] is 0.5 to 3. 5
2. The battery according to claim 1, characterized in that the chalcogen compound is a lithium cobalt oxide ($\text{Li}_{x}\text{CoO}_2$). 20
3. The battery according to claim 1, characterized in that the electrolytic salt is LiPF_6 . 25
4. The battery according to claim 1, characterized in that the dissolution amount of the electrolytic salt in the solvent mixture is 0.75 mol/l to 1.25 mol/l. 30
5. The battery according to claim 1, characterized in that the noncyclic carbonate is diethyl carbonate or diethyl carbonato. 35
6. The battery according to claim 1, characterized in that the cyclic carbonate is ethylene carbonate, propylene carbonate or butylene carbonate. 40
7. The battery according to claim 6, characterized in that the first nonaqueous solvent is a mixture of ethylene carbonate and propylene carbonate. 45
8. The battery according to claim 5 or 6, characterized in that the first nonaqueous solvent is a mixture of propylene carbonate and diethyl carbonate. 50
9. The battery according to claim 1, characterized in that the second nonaqueous solvent is 1,2-diethoxyethane or 1,2-dimethoxyethane. 55
10. The battery according to claim 1, characterized in that the amount of the second nonaqueous solvent in the solvent mixture is determined such that the mol ratio ([S]/[Li]) of the second nonaqueous solvent [S] to the lithium ions [Li] is 1 to 2.



F I G. 1



F I G. 2





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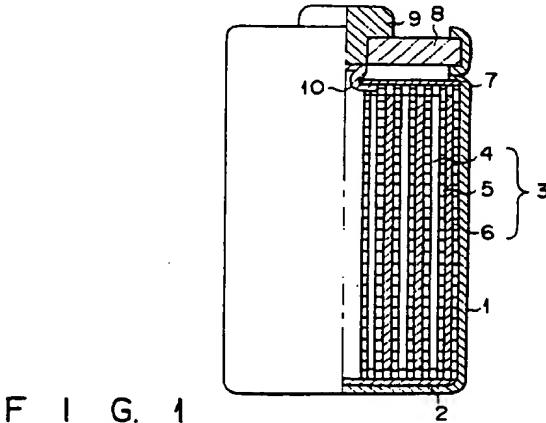
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(54) A nonaqueous electrolyte secondary battery.

(57) A nonaqueous electrolyte secondary battery having an enhanced capacity and a long charge/discharge cycle life is disclosed. The nonaqueous electrolyte secondary battery comprises a positive electrode (4) housed in a case (1) and containing a chalcogen compound as an active material, a negative electrode (6) arranged in the case (1) such that a separator (5) is sandwiched between the positive and negative electrodes (4, 6) and containing a carbonaceous material as an active material that absorbs and discharges lithium ions and a nonaqueous electrolyte contained in the case (1) and prepared by dissolving 0.5 mol/l to 1.5 mol/l of electrolytic salt selected from the group consisting of LiPF₆, LiBF₄, LiAsF₆ and LiCF₃SO₃ in a solvent mixture comprising at least one first nonaqueous solvent selected from the group consisting of noncyclic carbonate, cyclic carbonate, γ-butyrolactone and acetonitrile and at least one second nonaqueous solvent containing selected from the group consisting of 1,2-diethoxyethane, 1,2-dimethoxyethane, 1,2-ethoxymethoxyethane, 1,3-dimethoxypropane, diethylether and tetrahydrofuran, the amount of the second nonaqueous solvent in the solvent mixture being so determined that the mol ratio ([S]/[Li]) of the second nonaqueous solvent [S] to lithium ions [Li] is 0.5 to 3.





European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 91 30 8881

DOCUMENTS CONSIDERED TO BE RELEVANT									
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)						
P, X	EP-A-0 398 689 (KABUSHIKI KAISHA TOSHIBA) * column 5, line 52 - line 57 * * column 6, line 51 - column 7, line 17 * * claims 11-16 * ----	1,3,4,6, 7,9,10	H01M4/58 H03M10/40						
A	EP-A-0 249 331 (MITSUBISHI GAS CHEMICAL CO.) * column 5, line 45 - line 48 * * column 6, line 13 - line 36 * * column 13, line 10 - line 14 * * claim 1 * -----	1,3,4,6, 8							
TECHNICAL FIELDS SEARCHED (Int. Cl.5)									
H01M									
<p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of compilation of the search</td> <td style="width: 34%;">Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>27 FEBRUARY 1992</td> <td>ANDREWS M. P.</td> </tr> </table>				Place of search	Date of compilation of the search	Examiner	THE HAGUE	27 FEBRUARY 1992	ANDREWS M. P.
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CATEGORY OF CITED DOCUMENTS									
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document							